

What is claimed is:

1. A method for forming combinatorial libraries of supported metal-containing powders, the method comprising:

(i) preparing an array comprising a plurality of dispersions, each of the plurality of dispersions being prepared by a method comprising dispersing a particulate support in a solution, the solution comprising a solvent and a dissolved metal, wherein the volumetric ratio of the particulate support to the solvent is at least about 1:10;

(ii) removing heat concurrently from each of the plurality of dispersions in the array to precipitate the dissolved metal from the solution onto the particulate support; and

(iii) after step (ii), separating the particulate support from the solution for each of the plurality of dispersions in the array to yield an array comprising a plurality of supported metal-containing powders, each of the plurality of powders comprising the particulate support and a precipitated metal thereon.

2. The method of claim 1 further comprising, for each of the plurality of powders in the array, reducing the precipitated metal on the particulate support.

3. The method of claim 2 wherein the precipitated metal is reduced to its metallic oxidation state.

4. The method of claim 1 wherein the particulate support used to form one or more of the dispersions comprises a pre-deposited material selected from the group consisting of a pre-deposited metal compound, a pre-deposited metal in its metallic oxidation state, and combinations thereof, the method further comprising forming an alloy on the particulate support, the alloy comprising metals derived from the pre-deposited material and the precipitated metal.

5. The method of claim 1 wherein one or more of the dispersions is formed using a solution comprising a first dissolved metal and a second dissolved

metal, both of which are precipitated on the particulate support upon removal of heat from said dispersion.

6. The method of claim 5 further comprising forming an alloy on the particulate support, the alloy comprising metals derived from the first and second precipitated metals.

7. The method of claim 1 wherein each of the plurality of dispersions is within a container having an exterior and heat is removed from the dispersions in step (ii) by contacting the exterior of each container with a cooling medium.

8. The method of claim 7 wherein in step (iii) the separated solution is removed from each container.

9. The method of claim 7 wherein one of more of the containers has a cover that allows for a gas but substantially no particulate support to exit therefrom.

10. The method of claim 1 wherein, for one or more of the dispersions in the array, the volumetric ratio of particulate support to solvent is at least about 1:8.

11. The method of claim 1 wherein, for one or more of the dispersions in the array, the volumetric ratio of particulate support to solvent is at least about 1:5.

12. The method of claim 1 wherein, for one or more of the dispersions in the array, the volumetric ratio of particulate support to solvent is at least about 1:2.

13. The method of claim 1 wherein each of the plurality of dispersions has a viscosity that is at least about 5,000 mPa·s.

14. The method of claim 1 wherein, for each of the plurality of dispersions, the particulate support are uniformly dispersed in the solution.

15. The method of claim 1 wherein one or more of the plurality of dispersions is a suspension.

16. The method of claim 1 wherein the removal of heat from each of the plurality of dispersions freezes the solution.

17. The method of claim 1 wherein separation of the particulate support from the solution for each of the plurality of dispersions, after step (ii) is complete, is by filtration, evaporation, sublimation, or a combination thereof.

18. The method of claim 1 wherein separation of the particulate support from the solution for each of the plurality of dispersions, after step (ii) is complete, is by freeze-drying.

19. A method of forming a combinatorial library of supported metal-containing powders, the method comprising:

(i) preparing an array comprising a plurality of dispersions, each of the plurality of dispersions being prepared by a method comprising dispersing a particulate support in a solution, the solution comprising a solvent and a dissolved metal;

(ii) removing heat concurrently from each of the plurality of dispersions to precipitate the dissolved metal from the solution onto the particulate support and to freeze the solution, wherein heat is removed from each dispersion by contacting a container in which each of the plurality of dispersions is contained with a cryogenic liquid; and,

(iii) after step (ii) separating the particulate support from the solution for each of the plurality of dispersions by freeze-drying to yield a plurality of supported metal-containing powders in the array, each of the plurality of powders comprising the particulate support and a precipitated metal thereon.

20. The method of claim 19 further comprising, for one or more of the plurality of powders, reducing the precipitated metal on the particulate support.

21. The method of claim 20 wherein the precipitated metal is reduced to its metallic oxidation state.

22. The method of claim 20 wherein the precipitated metal on the particulate support for each of the plurality of powders has a deposit size that is less than about 20 nm.

23. The method of claim 20 wherein the precipitated metal on the particulate support for each of the plurality of powders has a deposit size that is between about 2 and about 3 nm.

24. The method of claim 19 wherein steps (i) and (iii) are also performed in the container.

25. The method of claim 24 wherein each of the plurality of containers has a cover that allows for a gas but substantially no particulate support to exit therefrom.

26. The method of claim 19 wherein the solvent is selected from the group consisting of water, an alcohol, acetic acid, carbon tetrachloride, ammonia, 1,2-dichloroethane, N,N-dimethylformamide, and formamide.

27. The method of claim 19 wherein the solvent comprises water.

28. The method of claim 19 wherein the dissolved metal for each of the plurality of dispersions is from a metal-containing compound selected from the group consisting of a metal sulfate, a metal nitrate, a metal nitrite, a metal oxalate, metal acetate, and metal formate.

29. The method of claim 19 wherein the dissolved metal for each of the plurality of dispersions is from an inorganic metal-containing compound.

30. The method of claim 19 wherein the particulate support in each of the plurality of dispersions is selected from the group consisting of carbon particulate support and electrically conductive polymer particulate support.

31. The method of claim 19 wherein the particulate support in each of the plurality of dispersions and powders resulting therefrom comprises a pre-deposited material selected from the group consisting of a pre-deposited metal compound, a pre-deposited metal in its metallic oxidation state, and combinations thereof, the method further comprising forming an alloy on the particulate support for each of the plurality of powders, each alloy comprising metals derived from the pre-deposited material and the precipitated metal.

32. The method of claim 31 wherein the loading of the pre-deposited material on the particulate support is up to about 90 weight percent.

33. The method of claim 31 wherein the loading of the pre-deposited material on the particulate support is between about 5 and about 60 weight percent.

34. The method of claim 31 wherein the pre-deposited material has a deposit size that is less than about 20 nm.

35. The method of claim 31 wherein the pre-deposited material has a deposit size that is between about 2 and about 3 nm.

36. The method of claim 31 wherein the alloy has a deposit size that is less than about 20 nm.

37. The method of claim 31 wherein the alloy has a deposit size that is between about 2 and about 3 nm.

38. The method of claim 19 wherein each of the plurality of dispersions is formed using a solution comprising a first dissolved metal and a second dissolved

metal, both of which are precipitated on the particulate support upon removal of heat from each of the plurality of dispersions.

39. The method of claim 38 further comprising, after step (iii), forming an alloy on the particulate support for each of the plurality of powders in the array, each alloy comprising metals derived from the first and second precipitated metals.

40. The method of claim 19 wherein the particulate support for each of the plurality of dispersions has an average size of at least about 100 nm.

41. The method of claim 19 wherein the particulate support for each of the plurality of dispersions has an average size that is between about 200 and about 300 nm.

42. The method of claim 19 wherein the particulate support for each of the plurality of dispersions comprise between about 1 and about 30 weight percent of each dispersion.

43. The method of claim 19 wherein the particulate support for each of the plurality of dispersions comprise between about 1 and about 10 weight percent of each dispersion.

44. The method of claim 19 wherein step (ii) comprises cooling concurrently each of the plurality of dispersions at a rate of at least about 20 °C/minute.

45. The method of claim 19 wherein step (ii) comprises cooling concurrently each of the plurality of dispersions at a rate between about 50 and about 100 °C/minute.

46. The method of claim 19 wherein the cryogenic liquid is at a temperature that is at least about 20 °C below the freezing point of the solvent portion.

47. The method of claim 19 wherein the cryogenic liquid is selected from the group consisting of liquid nitrogen, liquid hexane, liquid helium, liquid argon, an ice water/hydrous calcium chloride mixture, an acetone/dry ice mixture, and a diethyl ether/dry ice mixture.

48. A method for forming a combinatorial library of supported metal-containing powders, the method comprising:

(i) preparing an array comprising a plurality of dispersions, each of the plurality of dispersions being prepared by a method comprising dispersing a particulate support in a solution, the solution comprising a solvent and a dissolved metal;

(ii) removing heat concurrently from each of the plurality of dispersions to precipitate the dissolved metal from the solution onto the particulate support and to form a plurality of composites, each of the plurality of composites comprising the particulate support and the precipitated metal thereon within a matrix that comprises the solvent in a solid state; and

(iii) freeze-drying each of the plurality of composites to separate the particulate support from the solvent to yield a plurality of supported metal-containing powders, each of the plurality of powders comprising the particulate support and the precipitated metal thereon.

49. The method of claim 48 wherein the solvent is selected from the group consisting of water, an alcohol, acetic acid, carbon tetrachloride, ammonia, 1,2-dichloroethane, N,N-dimethylformamide, and formamide.

50. The method of claim 48 wherein the solvent comprises water.

51. The method of claim 48 wherein the dissolved metal for each of the plurality of dispersions is from a metal-containing compound selected from the group consisting of a metal sulfate, a metal nitrate, a metal nitrite, a metal oxalate, metal acetate, and metal formate.

52. The method of claim 48 wherein the dissolved metal for each of the plurality of dispersions is from an inorganic metal-containing compound.

53. The method of claim 48 wherein the particulate support in each of the plurality of dispersions is selected from the group consisting of carbon particulate support and electrically conductive polymer particulate support.

54. The method of claim 48 wherein the particulate support in each of the plurality of dispersions and powders resulting therefrom comprises a pre-deposited material selected from the group consisting of a pre-deposited metal compound, a pre-deposited metal in its metallic oxidation state, and combinations thereof, the method further comprising forming an alloy on the particulate support for each of the plurality of powders, each alloy comprising metals derived from the pre-deposited material and the precipitated metal.

55. The method of claim 48 wherein each of the plurality of dispersions is formed using a solution comprising a first dissolved metal and a second dissolved metal, both of which are precipitated on the particulate support upon removal of heat from each of the plurality of dispersions.

56. The method of claim 48 further comprising, after step (iii), forming an alloy on the particulate support for each of the plurality of powders in the array, each alloy comprising metals derived from the first and second precipitated metals.

57. The method of claim 48 wherein the particulate support for each of the plurality of dispersions comprise between about 1 and about 30 weight percent of each dispersion.

58. The method of claim 48 wherein the particulate support for each of the plurality of dispersions comprise between about 1 and about 10 weight percent of each dispersion.

59. The method of claim 48 wherein step (ii) comprises cooling concurrently each of the plurality of dispersions at a rate of at least about 20 °C/minute.

60. The method of claim 48 wherein step (ii) comprises cooling concurrently each of the plurality of dispersions at a rate between about 50 and about 100 °C/minute.

61. The method of claim 48 wherein the cryogenic liquid is at a temperature that is at least about 20 °C below the freezing point of the solvent portion.

62. The method of claim 48 wherein the cryogenic liquid is selected from the group consisting of liquid nitrogen, liquid hexane, liquid helium, liquid argon, an ice water/hydrous calcium chloride mixture, an acetone/dry ice mixture, and a diethyl ether/dry ice mixture.

63. The method of any one of claims 1, 19 or 48 wherein the array comprises a plurality of dispersions, each of the plurality of dispersions being at spatially discrete regions of a common library substrate.

64. The method of any one of claims 1, 19 or 48 wherein the array comprises a plurality of dispersions, each of the plurality of dispersions being in separate containers supported on a common library substrate at spatially discrete regions.

65. The method of claim 64 wherein each container is open-ended.

66. The method of claim 64 wherein each container is closed.
67. The method of claim 64 wherein each container is hermetically-sealed.
68. The method of claim 64 wherein the common library substrate comprises regions having a region density of not more than about one region per cm^2 .
69. The method of claim 63 wherein the common library substrate comprises regions having a region density of not more than about one region per cm^2 .
70. The method of claim 63 wherein the common library substrate is a microtiter plate comprising regions defined by wells having a region density of not more than about one region per cm^2 .
71. The method of one of claims 1, 19 or 48 further comprising varying the chemical or physical properties of the particulate supports, as compared between different dispersions of the array.
72. The method of one of claims 1, 19 or 48 further comprising varying the chemical composition, stoichiometry or concentration, or relative amounts of the dissolved metal in the solution, as compared between different dispersions of the array.
73. The method of one of claims 1, 19 or 48 further comprising varying the chemical composition of the solvent of the solution, as compared between different dispersions of the array.
74. The method of one of claims 1, 19 or 48 further comprising removing heat such that a rate at which each of the plurality of dispersions cools varies, as compared between different dispersions of the array.

75. The method of one of claims 1, 19 or 48 further comprising varying the period of time during which heat is removed from each of the plurality of dispersions, as compared between different dispersions of the array.

76. The method of one of claims 1, 19 or 48 wherein each of the plurality of dispersions of the array are prepared concurrently.

77. The method of one of claims 1, 19 or 48 wherein, following step (ii), separation of each solution and the particulate support having a metal precipitated thereon is performed concurrently.

78. The method of one of claims 18, 19 or 49 wherein freeze-drying is performed concurrently.

79. The method of one of claims 4, 6, 31, 39, 54 or 56 wherein each alloy is formed concurrently.

80. The method of one of claims 1, 19 or 48 wherein the step of removing heat from each of the plurality of dispersions is effected while each of the plurality of dispersions are at spatially discrete regions of a common library substrate.

81. The method of claim 80 wherein each of the plurality of dispersions are prepared on a universal common library substrate that is the same library substrate on which each of the plurality of dispersions resides during the step of removing heat from each of the plurality of dispersions.

82. The method of one of claims 18, 19 or 48 wherein the step of freeze-drying is effected while each of the plurality of dispersions are at spatially discrete regions of a common library substrate.

83. The method of claim 82 wherein each of the plurality of dispersions are prepared on a universal common library substrate that is the same library substrate on which each of the plurality of dispersions reside during the step of freeze-drying.

84. The method of one of claims 1, 19 or 48 wherein the step of separating the solution and the particulate support is performed at spatially discrete regions of a common library substrate.

85. The method of claim 84 wherein each of the plurality of dispersions are prepared on a universal common library substrate that is the same library substrate on which the step of separating the solution and the particulate support is performed.

86. The method of any one of claims 4, 6, 31, 39, 54 or 56 wherein each of the plurality of alloys is formed at spatially discrete regions of a common library substrate.

87. The method of claim 86 wherein each of the plurality of dispersions are prepared on a universal common library substrate that is the same library substrate on which each of the plurality of alloys is formed.

88. The method of any one of claims 1, 19 or 48 wherein said plurality of dispersions comprises at least about 5 dispersions.

89. The method of any one of claims 1, 19 or 48 wherein said plurality of supported metal-containing powders comprises at least about 5 powders.

90. Use of the method of any one of claims 1, 19 or 48 in a process for generating data for an array of supported catalysts, such as supported electrocatalysts.

91. A combinatorial library of supported metal alloy powders, the combinatorial library comprising:

an array comprising a plurality of supported metal alloy powder members, each of the plurality of supported metal alloy powders comprising:

a particulate support;

deposits comprising a metal alloy on the particulate support, wherein the metal alloy comprises a non-noble metal;

a loading of deposits on the particulate support of at least about 20 weight percent;

an average deposit size that is no greater than about 10 nm; and,

a deposit size distribution wherein at least about 70 percent of the metal alloy deposits are between about 50 and about 150 percent of the average metal alloy deposit size;

the plurality of supported metal alloy powder members of the array being different from each other with respect to one or more characterizing features selected from the group consisting of: (i) chemical or physical properties of the particulate support; (ii) chemical or physical properties of the metal alloy on the particulate support; (iii) the extent of loading of the deposits on the particulate support; and (iv) the average deposit size on the particulate support.

92. The library of claim 91 wherein the particulate support is organic.

93. The library of claim 92 wherein the particulate support is electrically conductive.

94. The library of claim 93 wherein the particulate support is selected from the group consisting of carbon supports and electrically conductive polymer supports.

95. The library of claim 94 wherein the particulate support is a carbon support.

96. The library of claim 91 wherein the loading of the deposits is between about 20 and about 60 weight percent of the particulate support.

97. The library of claim 91 wherein the loading of the deposits is between about 20 and about 40 weight percent of the particulate support.

98. The library of claim 91 wherein the average deposit size is no greater than about 5 nm.

99. The library of claim 91 wherein the deposit size is no greater than about 2 nm.

100. The library of claim 91 wherein the average deposit size is between about 5 and about 10 nm.

101. The library of claim 91 wherein the deposit size distribution is such that at least about 80 percent of the metal alloy deposits are between about 75 and about 125 percent of the average metal alloy deposit size.

102. An apparatus for combinatorially screening materials for use as a fuel cell electrode, the apparatus comprising:

an array comprising a plurality of fuel cell electrodes, each of the fuel cell electrodes comprising a supported electrocatalyst powder and an electrode substrate upon which the supported electrocatalyst powder is deposited, the supported electrocatalyst powder comprising:

a particulate support;

deposits comprising a metal alloy on the particulate support, wherein the metal alloy comprises a non-noble metal;

a loading of deposits on the particulate support of at least about 20 weight percent;

an average deposit size that is no greater than about 10 nm; and

a deposit size distribution wherein at least about 70 percent of the metal alloy deposits are between about 50 and about 150 percent of the average metal alloy deposit size;

the supported electrocatalyst powders of the plurality of the fuel cell electrodes of the array being different from each other with respect to one or more characterizing features selected from the group consisting of: (i) chemical or physical properties of the particulate support; (ii) chemical or physical properties of the metal alloy on the particulate support; (iii) the extent of loading of the deposits on the particulate support; (iv) the average deposit size on the particulate support; and (v) the deposit size distribution.